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September 26, 2005

Physical Review Letters

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Raman spectroscopy in hot compressed hydrogen and nitrogen - implications for the intramolecular potential

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Raman measurements of molecular hydrogen, deuterium, and nitrogen have been made under simultaneous conditions of high temperature and high static pressure. Measurements have been made on hydrogen and deuterium to 50 GPa and 1600 K, and on nitrogen to 50 GPa and 2000 K. In all three materials the familiar molecular stretching mode (vibron) is accompanied in the high temperature Raman spectra by one or more lower frequency components due to transitions from excited vibrational states. We find the frequency differences between these bands decreases with pressure, implying that the anharmonicity of the corresponding part of the intramolecular potential also decreases. This is accompanied by an increase of the measured linewidths that is consistent with a decrease of the depth of the potential and an approaching molecular dissociation.

PACS:

The atoms in diatomic homopolar molecules are strongly bonded by covalent interaction. The dissociation energy of these materials is correspondingly high (consider that of N₂ for example: ~ 9.7 eV). Nevertheless, when a collection of molecular oscillators is subjected to sufficiently high pressure one can expect molecular dissociation and transformation to a monatomic system (e.g. [Ashcroft]). This is a consequence of the electronic density redistribution that follows from the increasing overlap of the molecular wave functions, valence charge transfer and the modification of the effective intramolecular potential. Elucidation of the detailed nature of these transformations represents one of the most important problems of condensed matter physics and has implications for the ongoing search for metallic hydrogen as well as new energetic materials.

At low and room temperatures molecular phases of hydrogen and nitrogen persist as orientationally ordered crystalline substances at surprisingly high pressure (at least in the range of several Mbar [Goncharov-Loubeyre,Goncharov-Eremets]), the corresponding compressional work of which is comparable to the potential well depth [Ashcroft] of the individual oscillators at 1 bar. Much less is known concerning the stability of molecular solid and liquid phases under *simultaneous* conditions of high pressure and temperature. Shock-wave compression experiments have been almost the sole way to obtain experimental data under such conditions. The dissociation of H_2 and N_2 molecules and the formation of metallic states during shock-wave compression has been reported [Weir,Nellis]. Corresponding experiments under static conditions have been limited because of the difficulties of containing the sample, which becomes highly reactive and/or mobile [Zinn,Datchi,Gregoryanz]. Theoretical calculations were extensively used to explore the intramolecular bonding in hydrogen under extreme conditions using a mean-field approach [Ashcroft], and also effective potentials that include an electronic response [Nagao]. These calculations show that although the change of frequency of the intramolecular stretching mode, or “vibron” is very moderate over a wide pressure range (which is qualitatively consistent with experimental observation), the intramolecular potential nevertheless changes substantially at high densities (due to charge transfer), and the interactions between different proton pairs become important.

In this Letter we report Raman measurements of compressed hydrogen and nitrogen at temperatures above the corresponding melting curves. In contrast to previous investigations we probe the intramolecular bonding by observing vibrational transitions not only from the ground to the first excited state but also from the first excited state and

from higher excited states (which become populated due to thermal excitation). The frequencies of these transitions are uniformly lower than that corresponding to the transition from the ground vibrational state, which is a consequence of the anharmonicity of the effective interatomic potential. We do however find that as the pressure is increased these differences in frequency become smaller, implying that this anharmonicity decreases. We also find that the line widths of the corresponding bands broaden with pressure, consistent with an approaching molecular dissociation. Our preliminary report on nitrogen to lower pressure has been published in a conference proceedings [JLT].

We have performed the experiments using the laser-heated diamond anvil cell (DAC) in the manner described previously [water,JLT]. Nitrogen was loaded into the DAC cryogenically along with an iridium square of side of length of 40 μm , thickness of 5-10 μm and with a central hole of 5-10 μm . This square was used to absorb incident laser light and to thus consequently heat the sample material contained in the hole. In some experiments thin (<5 μm) alumina plates were positioned adjacent to the tips of the diamond anvils to function as thermal insulators, so the thermal gradients in the sample were minimized. Experiments with hydrogen isotopes were performed in two steps. First, thin aluminum plates (<20 μm) were loaded into the DAC along with liquid common, or heavy water, pressurized to between 5 and 20 GPa and then laser heated to temperatures exceeding 2000 K. This procedure initiated a predictable chemical reaction that yielded hydrogen or deuterium, and alumina as reaction products. We found that hydrogen isotopes accumulated in vesicles near areas of unreacted aluminum which thus permitted further laser heating. In the second stage of the experiment Raman spectra were collected

as a function of temperature (typically to 1600 K).. Thin iridium plates or powder were also occasionally included in the DAC cavity to enhance the laser heating efficiency. We found that the hydrogen isotopes often migrated during laser heating and that clathrates formed with unreacted water [Vos] upon cooling the samples (clathrates were easily identified because the corresponding vibron frequency is larger than that of the free isotope and also because of the appearance of higher frequency sidebands similar to those that have been observed in other hydrogen containing van-der-Waals compounds [Hemley].) We find that clathrates break down to release hydrogen when heated above approximately 1000-1200 K below 50 GPa, but remain stable at higher pressures and temperatures above 1500 K. (This may be related to the triple point on the water phase diagram that has recently been identified [water].) The results presented in this work refer to temperatures measured radiometrically and also obtained from the ratio of the Stokes-to-Antistokes Raman intensities. These two estimates were consistent within the mutual uncertainties (~ 100 K). Pressure was measured at room temperature using a ruby manometer before and after experiment and was assumed to be temperature independent [water, JLT].

Fig. 1 shows representative high-temperature Raman spectra. Prior to melting the Raman spectrum of nitrogen exhibits two major vibron bands (above 4 GPa) associated with molecules occupying nonequivalent crystallographic positions. Naturally, only one vibron mode is expected in the liquid state [Zinn]. In addition to this main vibron band the spectra of hot compressed nitrogen reveal a number of additional lower-frequency components whose intensities decreased with decreasing frequency (Fig. 1a,b). The frequency separations between these additional components were all approximately equal.

We observed a single lower-frequency component in hot hydrogen and deuterium (Fig. 1c,d). The intensities of these additional modes in all three materials increased with temperature according to the Boltzmann relation $I_{n,n+1} \sim (n+1) \exp(-\hbar\omega/kT)$, where n is the vibrational quantum number and ω is the vibrational frequency. It was encouraging to note that the application of this relation to the experimental intensities (Fig. 1) yielded temperatures that were in agreement with those obtained using the methods described earlier. This fact confirms the assignment of the additional modes to vibrational transitions from excited states (see also CARS study [Schmidt,Baer]). In the case of nitrogen, then, the transitions up to and from the third excited level (the “3,4” transition), were observed while only the 1,2 transition was observed in hydrogen and deuterium, in addition to the familiar 0,1 transition that was observed in all three. This distinction may be accounted for by considering the sizeable differences between the vibrational energy of nitrogen and those of the hydrogen isotopes, and also the fact that the measurements were made at similar temperatures.

Raman frequencies of the vibron modes of liquid nitrogen (at temperatures between 1500 and 1900 K) show a monotonic dependence on pressure to at least 50 GPa (Fig. 2a). Frequencies obtained using the CARS technique under static [Baer] and dynamic [Schmidt] conditions up to 20 GPa are mutually consistent but are slightly smaller than our values (Fig 2a). This discrepancy is unlikely to be a consequence of different experimental temperatures, since according to our results the temperature dependence of the nitrogen vibron is weak. We also clearly observe that the anharmonic shifts of the vibron frequencies corresponding to transitions from excited states become

smaller with pressure (Fig. 2b) – a new and unexpected observation. It is also worth noting that the vibron linewidth increases with pressure (Fig. 3b).

In hydrogen and deuterium the temperature dependence of the vibron frequency (a uniform softening) and the linewidth is much stronger than in nitrogen (Fig. 3). Moreover, these dependences become even stronger at higher pressure (see also [Gregoryanz]). We find that the vibron frequency depends strongly on temperature in the liquid state by comparing the vibron frequency just under the melting curve [Gregoryanz] with our measurements at higher temperature (Fig. 3). As a result, the frequency of the hydrogen vibron at high temperature passes through a maximum that is located at lower pressure compared with that observed at room temperature. The pressure dependence of the 1,2 transition is also nonmonotonic, the anharmonic shift, however, linearly decreases with pressure (Fig. 3b) and at a much faster rate than in the case of nitrogen. The vibron linewidth also increases with pressure (Fig. 3c). The results for deuterium are qualitatively similar, but the vibron softening and the rate of decrease of the anharmonic shift is smaller (Fig. 3b).

We now consider the implications for the intramolecular potential of the results just described. It has commonly been assumed that the overlap of individual oscillator wave functions remains small at moderate compression, although the parameters of the potential may be a function of density [Ashcroft]. We assume that the effect of pressure on the potential is to increase the electronic kinetic energy and by a value equal to the corresponding work done during the isothermal compression, A . This increase naturally tends to reduce the amount of energy required for molecular dissociation, D . [Ashcroft,LoubeyreNe]. We have been computed A using the equation of state of solids

at ambient temperature [Olijnyk,LoubeyreEOS] (we neglected the thermal expansion because no data is available). Compression to 50 GPa corresponds to approximately 0.8 and 1 eV per molecule additional electronic energy for nitrogen and the hydrogen isotopes, respectively.

A particularly convenient and illustrative model potential to employ in this situation is that proposed by Morse: $\Phi=D(\exp(2\alpha(r-r_m)-2\exp(\alpha(r-r_m)))$, where α is the range parameter and r_m is the position of the potential minimum. It has the advantage that it is analytically tractable [Landau, Hagelstein]. Also, in contrast to the simple harmonic oscillator the spacings between the corresponding eigenenergies decrease progressively and by a constant amount.

We estimate the relevant parameters of the Morse potential for nitrogen and the hydrogen isotopes as described below. We assume the potential depth at ambient pressure, D_0 , to be that of the empirical Rydberg-Klein-Rees (RKR) potential. Subtraction of our calculated value of A at each pressure from D_0 yields an estimate of D . To obtain alpha we note that for the Morse potential the frequency corresponding to the (0,1) transition is given by

$$\hbar\omega_{0-1}=2\alpha(D/2\mu)^{1/2} - \alpha^2/\mu,$$

where μ is the reduced mass. Experimentally determined frequencies together with our values for D are then used to determine α . Following [Ashcroft,Loubeyre91] we also determine D and α for hydrogen independently by solving simultaneously the corresponding equations for each isotope. The results of these procedures are shown in Fig. 4. We note first that the assumption concerning the decrease of D with the increase of A is justified for hydrogen in light of the good agreement obtained for the two distinct

approaches (Fig. 4a). The range parameter α is seen to increase monotonically for both nitrogen and the hydrogen isotopes (Fig. 4b), and again, in the case of hydrogen, the values obtained for α are consistent for the two approaches. Since it can be shown that the anharmonic shift of the vibrational transitions is $\hbar\Delta\omega=\alpha^2/\mu$ it is easy to see that an increasing α leads to an increasingly anharmonic potential. However, if we consider the *measured* anharmonic shift we get precisely the opposite result that is that the potential becomes increasingly *harmonic* (Fig. 4b). It is worth noting that at nearly ambient pressure both determinations of α yield nearly consistent results (Fig 4b) implying that under this condition the Morse potential is satisfactory, as expected.

In conclusion we have examined the intramolecular potentials of hot hydrogen, deuterium and nitrogen to a pressure of 50 GPa. On the basis of measured transitions from the ground and excited states of the molecular vibron we have found that in all three cases the potential become less anharmonic near the equilibrium position. Concomitantly, the increase of the linewidth of the vibron band indicates that the potential barrier for molecular dissociation decreases with compression. These effects are most pronounced in hydrogen because of the relatively high vibron energy (with respect to the potential well depth). Theoretical calculations of the intramolecular potential function under conditions when the individual molecular oscillators cannot be considered independent are necessary to fully understand the observed behavior.

Work at Lawrence Livermore National Laboratory was performed under the auspices of the University of California under DOE Contract No. W-7405-Eng-48.

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Figures.

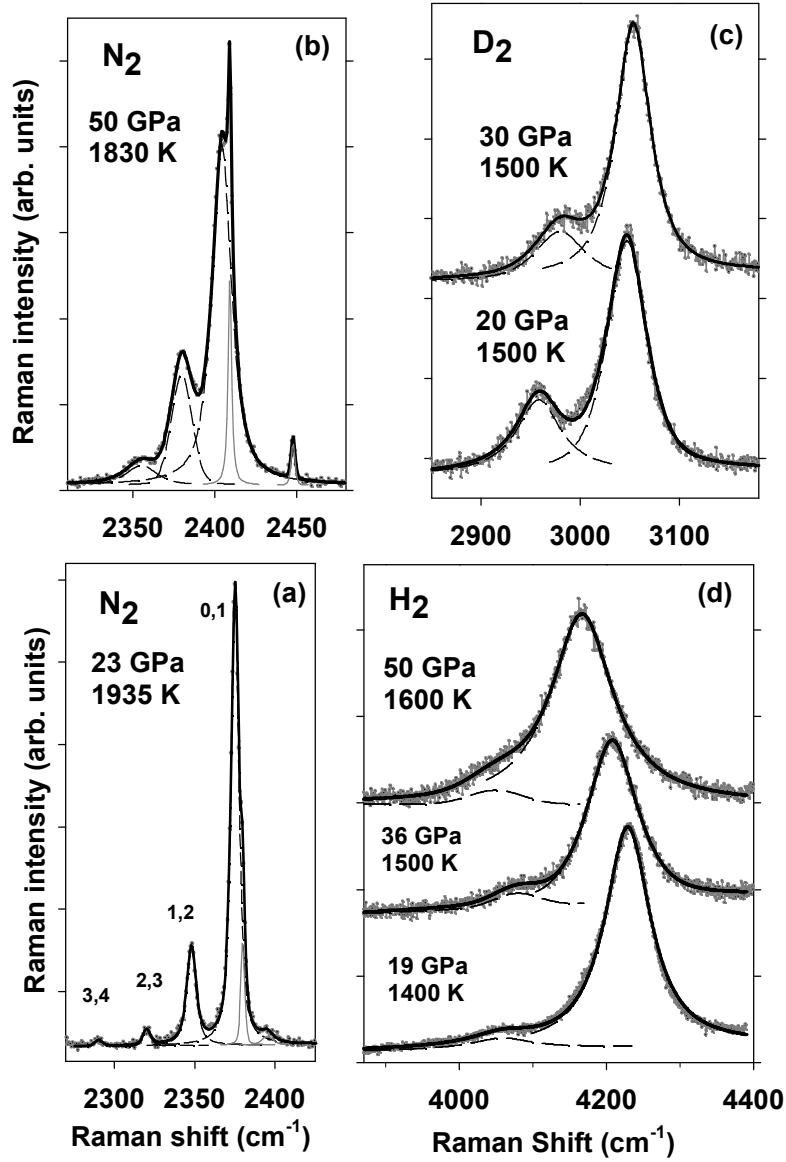


Figure 1. High temperature Raman spectra of hot nitrogen, hydrogen and deuterium at different pressures. Dotted grey line - experiment, black thick line – phenomenological

fit, dashed black and solid grey lines represent individual components used to fit the spectra. The spectra of nitrogen (a,b) have a contribution from the cooler part of the sample adjacent to the diamond anvil tips (solid grey lines).

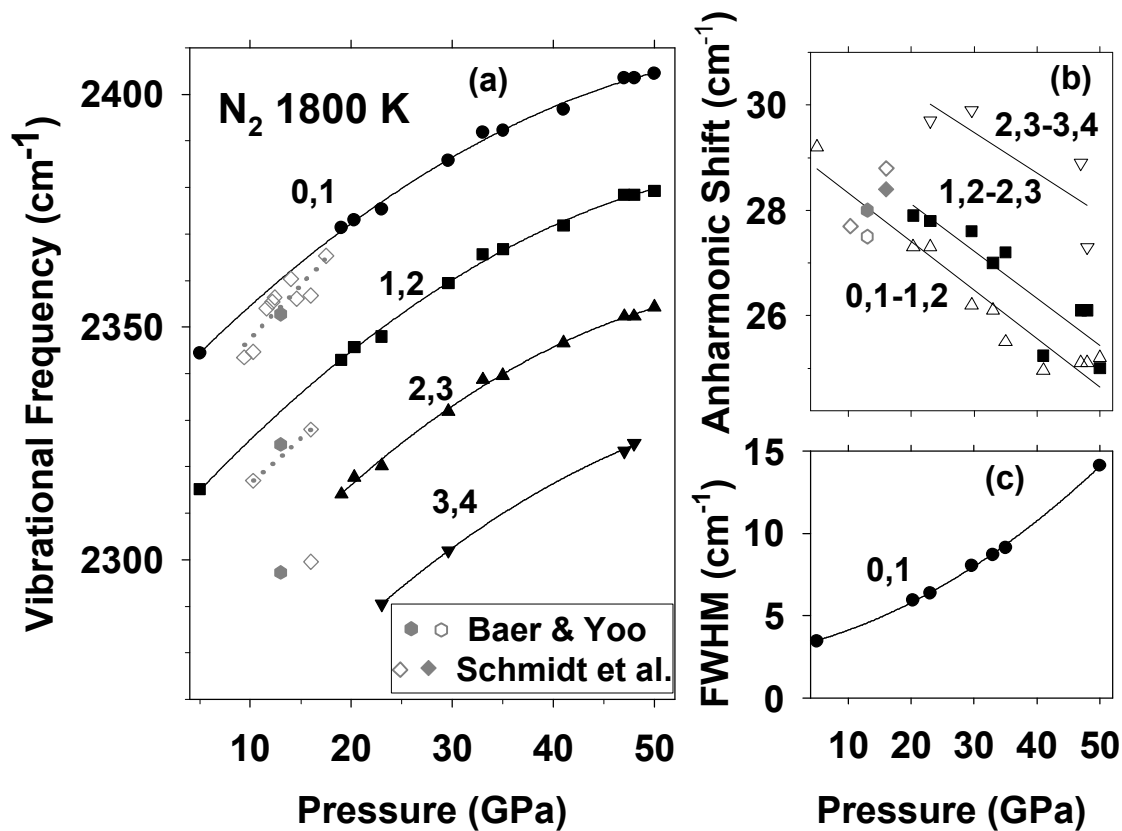


Figure 2. (a) Pressure dependences of measured vibron frequencies in nitrogen corresponding to transitions between vibrational levels n and $n+1$ ($n,n+1$), where n is the vibrational quantum number; (b) anharmonic frequency shifts (see text); (c) linewidth of the (0,1) transition. Grey symbols correspond to CARS data from Refs. [Baer,Schmidt] at 2000 K and 655-2400 K, respectively.

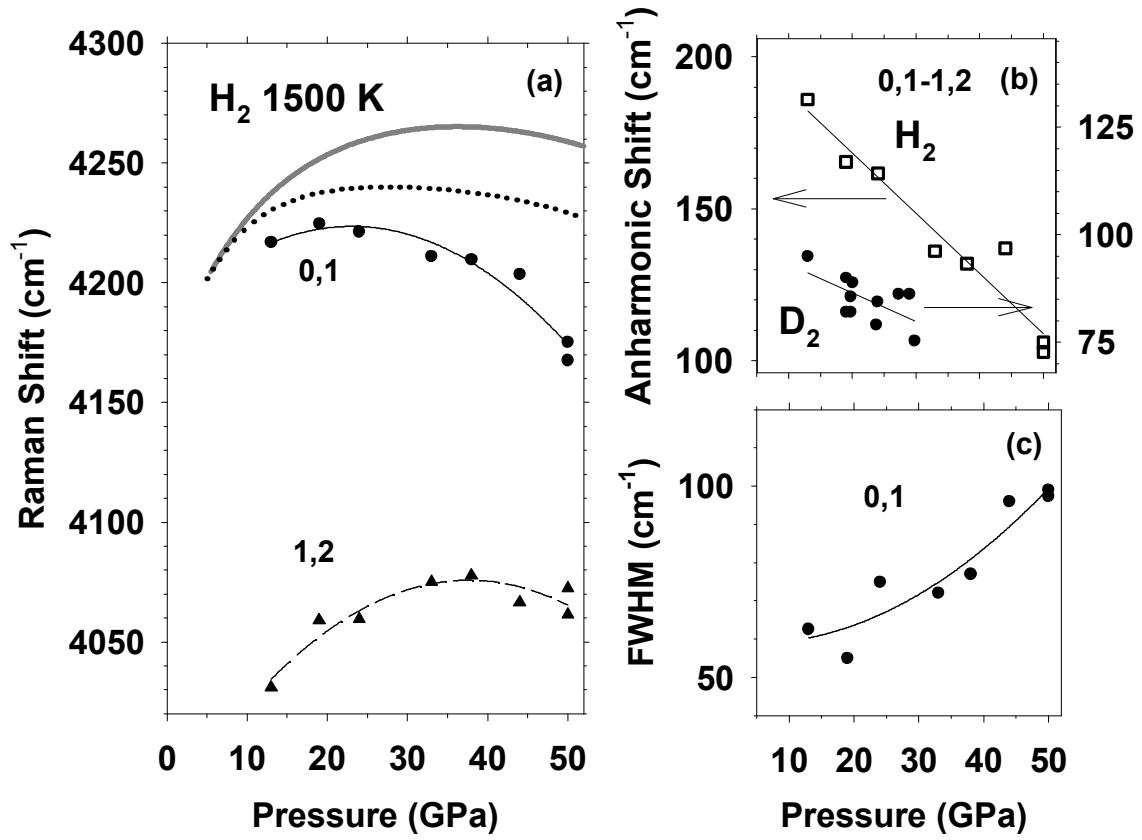


Figure 3. Same as in Fig. 2 but for hydrogen. Grey line in (a) – room temperature data [RMP]. Dotted line in (a) corresponds to the vibron frequency of solid hydrogen at the melting curve [Gregoryanz]. Fig. 3b compares the anharmonic frequency shifts for hydrogen and deuterium.

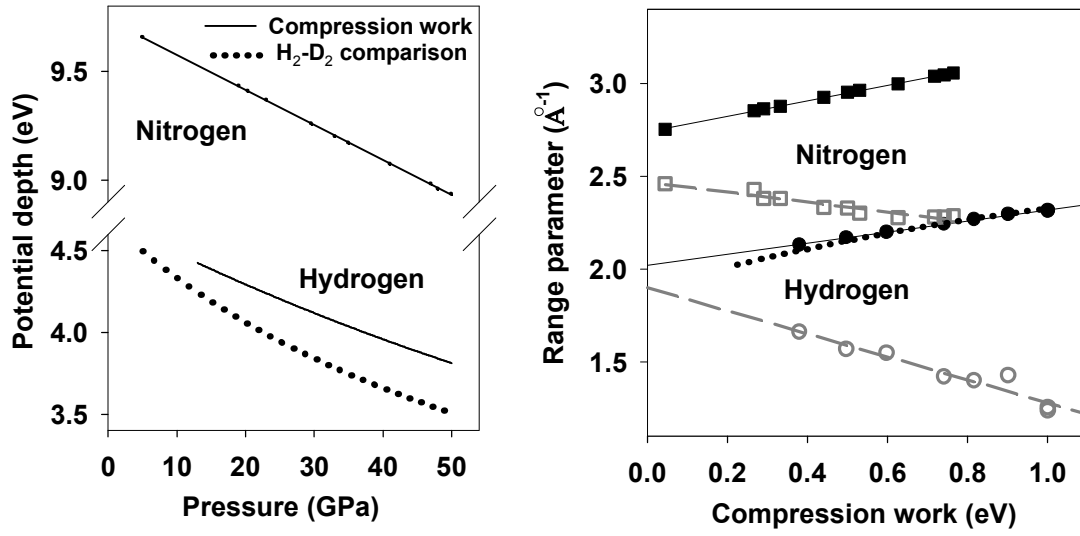


Figure 4. Parameters of the model Morse potential under compression. (a) Potential well depth (D). Solid lines: results obtained from calculation of compressional work. Dotted line: results obtained independently by comparing vibron frequencies of hydrogen and deuterium (see text). (b) Range parameter (α), Black symbols: α is determined from the frequency of the (0,1) vibrational transition; grey symbols: α is determined from the anharmonic shift associated with the transition from the first excited energy level. The dotted line was obtained in the same way as for Fig 4a.